6. TOXICITY

6.1 Introduction

This chapter presents the information that EPA has reviewed concerning the determination of toxicity to the receiving environment of various synthetic base fluids and the formulated synthetic-based drilling fluids (SBFs). This information includes data generated for toxicity requirements imposed on North Sea operators as well as experimental testing conducted by the oil and gas industry in the United States. Because the synthetic base fluids are water insoluble and the SBFs do not disperse in water as water-based drilling fluids (WBFs) do, but rather tend to sink to the bottom with little dispersion, most research has focused on determining toxicity in the sedimentary phase as opposed to the aqueous phase.

Since1984, EPA has used an aqueous phase toxicity test to demonstrate compliance with NPDES permits for the discharge of drilling fluids and drill cuttings. This aqueous phase test measures toxicity of the suspended particulate phase (SPP), and is often called the SPP toxicity test (see "Drilling Fluid Toxicity Test" 40 CFR 435, Subpart A, Appendix 2). SBFs have routinely been tested using the SPP toxicity test and found to have low toxicity (Candler et al., 1997). Rabke et al. 1998a, have recently presented data from an interlaboratory variability study indicating that the SPP toxicity results are highly variable when applied to SBFs, with a coefficient of variation of 65.1 percent. Variability reportedly depended on such things as mixing times and the shape and size of the SPP preparation containers. As part of the coastal effluent guidelines effort, published in December 1996, EPA identified the problems with applying the SPP toxicity test to SBFs due to the insolubility of the SBFs in water. (EPA, 1996).

North Sea testing protocols require monitoring the toxicity of fluids using a marine algae (*Skeletonema costatum*), a marine copepod (*Arcartia tonsa*), and a sediment worker (*Corophium volutator* or *Abra alba*). The algae and copepod tests are performed in the aqueous phase, whereas the sediment worker test uses a sedimentary phase. Again, because the SBFs are hydrophobic and do not disperse or dissolve in the aqueous phase, the algae and copepod tests are only considered appropriate for the water soluble fraction of the SBFs, while the sediment worker test is considered appropriate for the insoluble fraction of the SBFs (Vik et al., 1996a). As with the aqueous phase algae and copepod tests, the SPP toxicity test mentioned above is only relevant to the water soluble fraction of the SBFs (Candler et al., 1997).

Both industry and EPA have identified the need for more appropriate toxicity test methods for assessing the relative toxicities of various SBFs. EPA has recently begun a research project to determine the toxicity of synthetic and other oleaginous (oily) base fluids, and

influences of drilling fluid formulation and crude oil contamination on SBF toxicity. Results from this research are not yet available. Industry has sponsored and continues to sponsor research to evaluate and develop test procedures, with the goal of identifying an appropriate toxicity test method for SBFs as measured at the point of discharge. The toxicity data on SBFs and SBF base fluids that EPA was able to collect is summarized in Exhibit 6-1. The individual studies are summarized below.

6.2 Summaries of Identified Articles Containing Toxicity Information

The following two papers presented essentially the same data on *Ampelisca abdita* and *Corophuim volutator*. However, Still and Candler (1997) presented additional data not included by Candler et al., 1997. Therefore, we have included a summary of both papers.

Candler, J., R. Herbert and A.J.J. Leuterman. 1997. Effectiveness of a 10-day ASTM Amphipod Sediment Test to Screen Drilling Mud Base Fluids for Benthic Toxicity. SPE 37890.

The authors reported the results of a study sponsored by M-I Drilling Fluids. The study evaluated the use of the ASTM sediment toxicity test method E1367-92 for determining the toxicity base fluids used for SBFs and OBFs. The base fluids tested were a diesel oil (DO), an enhanced mineral oil (EMO), linear paraffin (LP), an internal olefin (IO) and a polyalphaolefin (PAO). The tests were conducted with two marine amphipods, *Ampelisca abdita* and *Corophium volutator*. The tests were conducted in two phases: 1) whole fluid was used to determine the range of toxicity to *A. abdita* and 2) base fluid was used in definitive tests to determine 10-day LC50 values for both test species. Chemical analyses for Total Petroleum Hydrocarbons (TPH) were used to determine actual exposure concentrations of the highest concentration of each test. For Phase 1 of the study, the amphipods were exposed to two concentrations (5,000 and 10,000 mg whole fluid/kg dry sediment). Ranking for toxicity, from most toxic to least toxic, at 5000 mg/kg sediment was: DO and EMO (zero percent survival in both tests), PAO (11 % survival), IO (32% survival), and LP (44% survival). Rankings at the 10,000 mg/kg sediment level, from most to least toxic, was: DO and EMO (O% survival), LP (8% survival), PAO (11% survival), and IO (25% survival). For Phase 2, the amphipods were exposed to definitive concentrations of a DO, EMO, IO and PAO. The toxicity ranking of the SBFs and OBFs were based on 10-day LC50 values. Those LC50 values, presented in decreasing toxicity (increasing LC50 values) for *A. abdita* tests were: EMO with an LC50 value of 557 mg/kg of sediment, DO with an LC50 value of 879 mg/kg, IO with an LC50 value of 3,121 mg/kg, and PAO with an LC50 value of 10,690 mg/kg. The LC50 values for *C. volutator* were: DO (840 g/kg), EMO (7,146 mg/kg), IO (>30,000 mg/kg), and PAO (>30,000 mg/kg). The authors stated that the study proved that the ASTM E1367-92 test methods and both of the test species can be used as screening tool for use with synthetic base fluids.

Exhibit 6-1. Reported Toxicities of Synthetic-Based Fluids (LC50s)

	Ampelisca abdita	*Leptocheirus plumulosus*	*Rhepoxynius abronius*	*Corophium volutator*	*Abra alba*	*Skeletonema costatum*	*Acartia tonsa*	*Fundulus grandis*
BASE FLUID - Natural Sediment								
Diesel Candler, 1997 Rabke, 1998b Still, 1997	879 mg/kg 1.0 ml/kg 0.7 ml/kg	850 mg/kg	24 mg/kg	840 mg/kg				
EMO Candler, 1997 Still, 1997	557 mg/kg	251 mg/kg	239 mg/kg	7146 mg/kg				
IO Candler, 1997 Rabke, 1998b Vik, 1996 Still, 1997	3121 mg/kg 4.0 ml/kg 3.0 ml/kg	3.7 ml/kg 2,944 mg/kg	299 mg/kg	>30,000mg/kg 7,100 mg/l	300 mg/l	2,050 mg/l	>10,000 mg/l	
PAO Candler, 1997 Rabke, 1998b Vik, 1996 Still, 1997	10,690 mg/kg 13.4 ml/kg 12.5 ml/kg	9,636 mg/kg	975 mg/kg	>30,000mg/kg 12.0 ml/kg 3.0 ml/kg	7,900 mg/l	3,900 mg/l	>50,000 mg/l	
Ester Vik, 1996a					>100,000 mg/l	60,000 mg/l	50,000 mg/l	
Acetal Vik, 1996a					549 mg/l	>100,000 mg/l	>100,000 mg/l	
LAO Vik, 1996a					1,021 mg/l	>10,000 mg/l	>10,000 mg/l	
BASE FLUID - Formulated Sediment								
Diesel Rabke, 1998b		1.0 ml/kg 0.7 ml/kg						

Exhibit 6-1. Reported Toxicities of Synthetic-Based Fluids (LC50s; continued)

	Ampelisca abdita	*Leptocheirus plumulosus*	*Rhepoxynius abronius*	*Corophium volutator*	*Abra alba*	*Skeletonema costatum*	*Acartia tonsa*	*Fundulus grandis*
WHOLE FLUID - Natural Sediment								
Diesel Rabke, 1998b	1.5 ml/kg	9.4 ml/kg						
IO Rabke, 1998b Friedheim et al., 1996	1.5 ml/kg	2.3 ml/kg		7,131 mg/kg	303 mg/kg			
PAO Rabke, 1998 Jones, 1991 Friedheim et al., 1996 Vik, 1996a	3.7 ml/kg	36.5 ml/kg		>10,000 mg/kg >10,000 mg/l	572 mg/kg 7,000 mg/l	82,400 mg/l	>50,000 mg/l	>8.4% TPH
Ester Vik, 1996a							34,000-145,000 mg/l	>50,000 mg/l
LAO Friedheim et al., 1996				1,268 mg/kg	277 mg/kg			
WHOLE FLUID - Formulated Sediment								
Diesel Rabke, 1998b		2.9 ml/kg 1.7 ml/kg 0.7 ml/kg 1.3 ml/kg						
IO Rabke, 1998b Hood, 1997	3.6 ml/kg	2.5 ml/kg 2.7 ml/kg 10.5 ml/kg 2,279 mg/kg 4,498 mg/kg 2,245 mg/kg 1,200 mg/kg 943 mg/kg						

Exhibit 6-1. Reported Toxicities of Synthetic-Based Fluids (LC50s; continued)

	Ampelisca abdita	***Leptocheirus plumulosus***	***Rhepoxynius abronius***	***Corophium volutator***	***Abra alba***	***Skeletonema costatum***	***Acartia tonsa***	***Fundulus grandis***
PAO Rabke, 1998b		<2.5 ml/kg						
WHOLE FLUID -No Sediment								
	Mysidopsis bahia							
IO Rabke, 1998a Hood, 1997	221,436 - >1,000,000 ppm (SPP) 56,500 - >1,000,000 ppm (SSP)							

Still, I. and J. Candler. 1997. Benthic Toxicity Testing of Oil-Based and Synthetic-Based Drilling Fluids. Eighth International Symposium on Toxicity Assessment. Perth, Western Australia. 25-30 May 1997.

A two phase sediment toxicity study was conducted to examine the applicability of established sediment toxicity test methods for synthetic base fluids and SBFs. During Phase I, the marine amphipod *Ampelisca abdita* was tested with one drilling fluid formulation dosed individually with the following five base fluids: a diesel oil (DO), an enhanced mineral oil (EMO), a linear paraffin (LP), an internal olefin (IO) and a polyalphaolefin (PAO). Testing during Phase I served as rangefinders, with test concentrations of 5,000 and 10,000 mg drilling fluid/kg dry sediment. Enhanced mineral oil and diesel were the most toxic for both concentrations. The toxicity ranking (most toxic to least toxic) for the SBFs at 5,000 mg/kg were PAO, IO and LP. The toxicity ranking (most toxic to least toxic) for the SBFs at 10,000 mg/kg were LP, PAO, and IO. For Phase II, definitive sediment toxicity tests were conducted. LC50 values were determined for EMO, DO, IO and PAO base fluids, using four marine amphipods: *Ampelisca abdita, Corophium volutator, Rhepoxynius abronius,* and *Leptocheirus plumulosus*. For *Ampelisca abdita,* the toxicity ranking (most toxic to least toxic) and corresponding LC50 values were: EMO (557 mg/kg); DO (879 mg/kg); IO (3,121 mg/kg); and PAO (10,680 mg/kg). For *Corophium volutator,* the toxicity ranking (most toxic to least toxic) and corresponding LC50 values were: DO (840 mg/kg); EMO (7,146 mg/kg); IO (>30,000 mg/kg); and PAO (>30,000 mg/kg). For *Rhepoxynius abronius* the toxicity ranking (most toxic to least toxic) and corresponding LC50 values were: DO (24 mg/kg); EMO (239 mg/kg); IO (299 mg/kg); and PAO (975 mg/kg). For *Leptocheirus plumulosus,* the toxicity ranking (most toxic to least toxic) and corresponding LC50 values were: EMO (251 mg/kg); DO (850 mg/kg); IO (2,944 mg/kg); and PAO (9,636 mg/kg). These results were ranked against the UK Offshore Chemical Notification Scheme (OCNS), which includes sediment testing as well as biodegradation and bioaccumulation in the ranking procedure. Using the OCNS classification, the results of this study ranked the based fluids, from most toxic to least toxic, as: diesel, enhanced mineral oil, IO and PAO.

Rabke S. et al. 1998a. Interlaboratory Comparison of a 96-hour Mysidopsis bahia Bioassay Using a Water Insoluble Synthetic-Based Drilling Fluid. Presented at 19th Annual Meeting of Society of Environmental Toxicology and Chemistry. Charlotte, NC 1998.

The authors conducted an interlaboratory variability study with six different laboratories using the SPP toxicity test with a synthetic-based drilling fluid (SBF). The purpose was to determine the variability associated with this test method when applied to SBFs. A subsample of an internal olefin SBF was shipped to the individual laboratories where the SPP test was conducted. Results were reported in ppm (vol:vol) of SPP and ranged from 221,436 to >1,000,000 ppm. The coefficient of variation was 65.1 %.

Rabke, S. and J. Candler. 1998b. Development of Acute Benthic Toxicity Testing for Monitoring Synthetic-Based Muds Discharged Offshore. Presented at IBC Conference on Minimizing the Environmental Effects of Offshore Drilling, Houston Texas, February 9, 1998.

The authors used the ASTM E1367-92 method to determine the toxicity of synthetic-based drilling fluids (SBFs) and oil-based drilling fluids (OBFs) to the marine amphipods *Ampelisca abdita* and *Leptocheirus plumulosus*. The authors examined the variability of the test, including variability due to test organisms. The authors used formulated sediments in place of natural sediments to evaluate their use in marine sediment testing. However, concurrent tests were conducted using natural sediment as a control. The test species were exposed to varying concentrations of diesel oil (DO), polyalphaolefin (PAO) and internal olefin (IO). The authors concluded that using formulated sediments and whole fluids decreased the usefulness of the test method as a screening tool; PAO synthetic-based drilling fluids appeared to be as toxic as diesel in the whole fluid/formulated sediment test; and formulated sediment gave acceptable control survival although it reduced the discriminatory power of the tests. The results of the study are presented in Exhibit 6-1.

Jones, F.V., J.H. Rushing and M.A. Churan. 1991. The Chronic Toxicity of Mineral Oil-Wet and Synthetic-Wet Cuttings on an Estuarine Fish, Fundulus grandis. *SPE 23497.*

The authors determined the toxic effects of cuttings associated with a mineral oil-based drilling fluid (OBF-cuttings) and a poly alpha oelfin (PAO) synthetic-based drilling fluid (PAO-SBF-cuttings) to an estuarine fish, the mud minnow, *Fundulus grandis*. Unaltered cuttings were dried and crumbled to a uniform state and divided in half. The cuttings were then hot rolled with the appropriate amounts of each drilling fluid to obtain concentrations of 1%, 5%, and 8.4% oil on wet cuttings, based on retort measurements. Before distributing the fish in test containers, the fish were anesthetized with 2.5 ppt quinaldine, then measured for weight and length. The fish were allowed to recover in fresh seawater before placement in test containers. Contaminated cuttings were layered (approximately 3.8 cm thick) into tanks, then covered with seawater. Each tank received seawater flow at a rate of 28.5 ml/2 minute intervals. The fish were exposed for a total of 30 days. Fish were randomly removed from each tank on Day 15 for length and weight measurements. The authors also sacrificed the fish for bioaccumulation measurements; no data were provided in this paper. (However, see Chapter 7 for a discussion of Rushing et al., 1991, a companion paper containing procedural details.) At Day 30 the remaining fish were measured for weight and length. The authors concluded that neither the mineral oil-based nor synthetic-based drilling fluids affected growth of the fish based on percentage growth. However, the overall growth of the control and 5% PAO-SBF cuttings-exposed fish at Day 15 and Day 30 were significantly greater than fish exposed to all other treatments.

Vik, E.A., S. Dempsey, B. Nesgard. 1996a. Evaluation of Available Test Results from Environmental Studies of Synthetic Based Drilling Muds. OLF Project, Acceptance Criteria for Drilling Fluids. Aquateam Report No. 96-010.

The authors provided a summary for tests conducted with unused base fluids and whole SBFs. However, the authors did not cite sources for the data, leaving one to assume the work was conducted by their laboratory. The authors state that the North Sea test organisms were a marine algae (*Skeletonema costatum*), a marine copepod (*Acartia tonsa*), and a sediment worker (*Corophium volutator*, or *Abra alba*). The authors consider that algae and copepods are relevant for the water soluble fraction tests and sediment workers are relevant for testing the non-soluble fraction. The authors further state that the algae has been the most sensitive of three species in controlling the toxicity of discharged fluids.

Montgomery, R. 1998. Memorandum to J. Daly, EPA, Regarding Draft API Sediment Toxicity Protocol for Use With Synthetic-Based Drilling Fluids. December 11, 1998. Plus attachments.

Work for this report is in progress, therefore detailed data will not be presented here. However, there are trends that appear worth reporting. API is sponsoring a research study to evaluate the appropriateness of sediment toxicity tests with *Leptocheirus plumulosus, Ampelisca abdita,* and *Mysidopsis bahia* as applied to SBFs and OBFs. The API research is also evaluating the MICROTOX test. Phase 1 of the study compared rangefinding results with whole fluids mixed in formulated sediments. Trends indicated sediment toxicity of the synthetic-based fluids did not differ much (i.e., by a factor of <2X) when compared to sediment toxicity of an OBF based on diesel oil. Phase 2 was conducted with the same species and whole fluids mixed in natural sediments. The trend was that sediment toxicity of the SBFs was slightly less (i.e., by a factor of 2-3X) when compared to sediment toxicity of OBFs. Another trend is the loss of discriminatory power between sediment toxicity of OBFs and SBFs. Results of the tests with natural sediments appeared to have better discriminatory power over the results of tests with formulated sediments. Both industry and EPA are currently investigating methods to discriminate sediment toxicity of SBFs and OBFs.

Hood, C. 1997. Unpublished Data Received By J. Daly (U.S. EPA) July 9,1997 from C. Hood, Baker Hughes INTEQ.

Unpublished data was provided by Ms. Cheryl Hood of Baker Hughes INTEQ, on the toxicity of four synthetic-based drilling fluids (SBFs) to the mysid, *Mysidopsis bahia* and the amphipod, *Leptocheirus plumulosus*. The 96-h LC50 for the mysids ranged from 14,600 to >500,000 ppm SPP and the 10-d LC50 for the amphipod ranged from 943 to 4498 mg SBF/kg dry sediment.

6.3 Summary

Although there are data available on the toxicity of both SBFs and base fluids from the North Sea and United States, the information is insufficient to draw meaningful conclusions other than broad generalizations. Also, little is known about the influence of the organics in either natural sediments or formulated sediments on the toxicity of these fluids. However, with the limited data, several assumptions can be made.

(1) North Sea amphipods appear to be less sensitive to synthetic base fluids than those amphipods currently used in US testing.
(2) Synthetic base fluid toxicity appears to show greater discriminatory power versus diesel toxicity than does SBFs toxicity.
(3) Discriminatory power seems to be diminished with the use of formulated sediments.
(4) Mysid SPP testing does not appear to be a relevant test method for these fluids.

Because data are limited, EPA and industry are continuing to gather information on sediment toxicity through ongoing research. Industry is currently evaluating sediment test methods, using formulated sediments and species sensitivities. EPA is beginning research on the toxicity of synthetic base fluids and the factors that influence the toxicity of these synthetic base fluids (as well as the biodegradation and bioaccumulation of synthetic base fluids). The goal of EPA research is to restore discriminatory power to discern the differences in toxicity between diesel oil, mineral oil, and synthetic base fluids. Because the current, examined amphipod test species are not indicating sufficient discriminatory power, EPA may further consider using other test organisms, such as polychaetes.

7. BIOACCUMULATION

7.1 Introduction

One factor to be considered in assessing the potential environmental impacts of discharged drilling fluids and drill cuttings is their potential for bioaccumulation. This chapter presents the information that EPA has gathered concerning the bioaccumulation of oleaginous base fluids, including the synthetic base fluids and mineral oil.

The information that EPA identified was provided by oil and gas operators and by oilfield chemical (drilling mud) suppliers. Much of this information is in the public domain. However, only a minimal amount can be found in peer reviewed publications. Most of the available information has been developed by mud suppliers to provide information to government regulators to assess the acceptability of these materials for discharge into the marine environment.

7.2 Summary of Data

The available information on the bioaccumulation potential of synthetic base fluids is scant, comprising only a few studies on octanol:water partition coefficients (P_{ow}) and two on tissue uptake in experimental exposures [only one of which derived a bioconcentration factor (BCF)]. The P_{ow} represents the ratio of a material that dissolves or disperses in octanol (the oil phase) versus water. The P_{ow} generally increases as a molecule becomes less polar (more hydrocarbon-like). The available information on the bioaccumulation potential of synthetic base fluids covers only three types of synthetics: an ester (one studies), internal olefins (IO; three studies), and poly alpha olefins (PAO; four studies). One study included a low toxicity mineral oil (LTMO) for comparative purposes. This limitation with respect to the types of synthetic base fluids tested is partially mitigated by the fact that these materials represent the more common of synthetic base fluid types currently in use in drilling operations.

These limited data suggest that synthetic base fluids do not pose a serious bioaccumulation potential. Despite this general conclusion, existing data cannot be considered sufficiently extensive to be conclusive. This caution is specifically appropriate given the wide variety of chemical characteristics resulting from marketing different formulations of synthetic fluids (i.e., carbon chain length or degree of unsaturation within a fluid type, or mixtures of different fluid types). Additional data should be obtained both for the purpose of confirming what is known about existing fluids and to ensure completeness and currency with new product development.

The data that EPA identified concerning the bioaccumulation potential of synthetic base fluids are summarized in Exhibit 7-1. Nine reports provided original information. This information consisted of P_{ow} data (based on calculated or experimental data), dispersibility data, or subchronic exposure of test organisms to yield data for calculating BCFs or assessing uptake. log P_{ow} values less than three or greater than seven would indicate that a test material is not likely to bioaccumulate (Zavallos et al., 1996).

For PAOs, the log P_{ow}s reported were >10, 11.9, 14.9, 15.4, and 15.7 in the four studies reviewed. The three studies of IOs that were reviewed reported log P_{ow}s of 8.57 and >9. The ester was reported to have a log P_{ow} of 1.69 in the one report in which it was tested. A log P_{ow} of 15.4 was reported for an LTMO. The only BCF reported was calculated for IOs; a value of 5.4 l/kg was determined. In 30-day exposures of mud minnows (*Fundulus grandis*) to water equilibrated with a PAO- or LTMO-coated cuttings, only the LTMO was reported to produce adverse effects and tissue uptake/occurrence. Growth retardation was observed for the LTMO and LTMO was observed at detectable levels in 50% of the muscle tissue samples examined (12 of 24) and most (19 of 24) of the gut samples examined. The PAO was not found at detectable levels in any of the muscle tissue samples and occurred in only one of twenty-four gut samples examined.

7.3 Summaries of Identified Reports Containing Bioaccumulation Information

Friedheim, J.E. et al. 1991. An Environmentally Superior Replacement for Mineral-Oil Drilling Fluids. SPE 23062. Presented at the Offshore Europe Conference, Aberdeen, September 3-6, 1991.

Bioaccumulation studies were conducted on both the PAO-base fluid and the PAO-based SBF. The calculated octanol/water partition coefficient for the PAO gives a log P_{ow} of 15.4. The authors concluded the PAO was not expected to bioaccumulate in aquatic species for a variety of reasons. The authors base their projection on data that indicate gill uptake of xenobiotics increases with increasing lipophilicity up to about a log P_{ow} of 7, beyond which there exists an inverse relationship between lipophilicity and bioconcentration. Thus, these authors believe that there appears to be a cut-off point in water solubility (or lack thereof) beyond which compounds cannot move past the aqueous diffusion layer present at the water/gill interface; a similar scenario accounts for a decreased absorption of hydrophobic chemicals in fish intestine. Therefore, Friedheim et al. concluded the physico-chemical properties of the PAO (i.e., low water solubility) would prohibit it from passing freely into aquatic species and bioaccumulating. PAOs are highly lipid soluble, and thus Friedheim et al. believe they are likely to be absorbed into the organic fraction of the sediment or onto suspended organic solids in the aquatic environment. These authors postulate that the PAO either would not be bioavailable (due to

Exhibit 7-1. Bioaccumulation Data for Synthetic Fluids and Mineral Oil Muds

Type of Synthetic Base Fluid or LTMO	Parameter Determined	Reference
PAO	log P_{ow}: 15.4 (calculated)	Friedheim et al., 1991
PAO	log P_{ow}: >10 (calculated)	Leutermann, 1991
PAO	log P_{ow}: 14.9 - 15.7 (measured)	Schaanning, 1995
PAO	log P_{ow}: 11.9 (measured)	Zevallos et al., 1996
IO	log P_{ow}: > 9	Environment & Resource Technology, Ltd., 1994a
IO	log P_{ow}: 8.57	Zevallos et al., 1996
Ester	log P_{ow}: 1.69	Growcock et al., 1994
LTMO	log P_{ow}: 15.4	Growcock et al., 1994
various	dispersibility: ranking = ester> di-ether >> detergent alkylate > PAO > LTMO	Growcock et al., 1994
IO	10-day uptake; 20-day depuration exposure gave log BCF: 5.37 (C16 forms); 5.38 (C18 forms)	Environment & Resource Technology, Ltd., 1994b
PAO	Uptake: no measured uptake in tissues after 30-day exposure; presence noted in 1 of 24 gut samples	Rushing et al., 1991
LTMO	Uptake: after 30-day exposure, detectable amounts in 50% of tissues analyzed (12 of 24) and 19 of 24 gut samples examined	Rushing et al., 1991
PAO	Subchronic effects: equal or better growth vs controls	Jones et al., 1991
LTMO	Subchronic effects: retarded growth vs controls	Jones et al., 1991

Abbreviations: PAO: poly alpha olefin; IO: internal olefin; LTMO: low toxicity mineral oil

sequestration by the sediment) or would not be able to pass through the gill (or intestine) due to the molecular size of the “suspended particle,” (which is likely referring to the adsorption of the PAO to the suspended organic solids to which the authors referred earlier).

Leuterman, A.J.J. 1991. Environmental Considerations in M-I Product Development Novasol/Novadril. M-I Drilling Fluids Co., January 15, 1991.

Although Novasol [a PAO] is highly lipid soluble, with a calculated octanol/water partition coefficient (log P) of >10.0, it was not expected by this author to bioaccumulate in aquatic species. Leuterman presented several reasons he considered well-documented. These reasons include the following:

1. High molecular weight, low water soluble polymers are thought not to pass biological membranes due to molecular volume considerations.

2. Highly lipophilic chemicals in aquatic systems are likely to absorb and partition into the organic fraction, in this case the organic fractions of the drilling fluid. In this arrangement the chemical constituent would not be bioavailable for absorption due to sequestration in the drilling fluid and cuttings or would not be able to pass through the gill or intestine, if ingested, due to the molecular size of the chemical constituent.

3. Gill uptake of xenobiotics increases with increasing lipophilicity up to about log P of 7. Beyond this level there exists an inverse relationship between lipophilicity and bioconcentration. Toxicokinetically this reduction apparently results from a decrease in the magnitude of the uptake rate constant. There appears to exist a cut-off point in the water solubility, i.e., the lack of, beyond which compounds cannot move past an aqueous diffusion layer present at the water/gill interface. A similar scenario accounts for decreased absorption of hydrophobic chemicals in fish intestines. Since transport into biological membranes requires, in most cases, that the xenobiotic be available in a dissolved form, the physico-chemical properties of Novasol, i.e., low water solubility, would prevent its passage into aquatic species and thence bioaccumulate.

4. If the base fluid did pass into the aquatic species, aquatic animals have the ability to metabolize xenobiotics through various enzyme systems located primarily in the intestine and liver. Once metabolized, these metabolites are normally of a more water soluble form, i.e., hydroxylated products, and are eliminated from the organism and not accumulated.

To confirm the expected low bioavailability of Novasol, M-I conducted a thirty (30) day bioaccumulation test using the mud minnow *Fundulus grandis*. This author states that preliminary results of this test reveal no detectable amount of the material, or its degradation products, in the tissue or organs of the test animals. In fact, the test animals showed no ill effect, no deformities and no reduced growth rates. No data are provided, however.

Friedheim, J.E. and R.M. Panternuehl. 1993. Superior Performance With Minimal Environmental Impact: A Novel Nonaqueous Drilling Fluid. SPE/IADC 25753. presented at the SPE/IADC Drilling Conference, Amsterdam, February 23-25, 1993.

Both an octanol/water partition coefficient determination and actual laboratory testing with fish were discussed to describe the potential for bioaccumulation of the PAO system. The authors cite earlier reports (Friedheim et al. 1991), in which the partition coefficient (log P_{ow}) for the PAO is 15.4. This high value along with the large molecular weight of the material led the authors to conclude the PAO should not accumulate in aquatic life. These arguments are based on knowledge of gill uptake of xenobiotics and absorption of hydrophobic chemicals in intestines of fish. The authors' conclusion is that the physico-chemical properties of the PAO would prohibit it from passing freely into aquatic species and bioaccumulating. Also, previous laboratory bioaccumulation test results (Rushing et al., 1991) using *Fundulus grandis* (mud minnow) were cited to support the arguments presented above.

Schaanning, M.T. 1995a. Evaluation of Overall Marine Impact of the Novadril Mud Systems. NIVA Report 0-95018.

The ICI Brixham Laboratory estimated that log Pow = 14.9-15.7 for a PAO product coded AB-5243-SO. This product was, however, composed of 65% of a synthetic hydrocarbon having a chain length of 22 carbon atoms (C22), 20% C32, and 15% C42 and C52 oligomers, neither of which were predominant components of the Novasol I and Novasol II base fluids. Measured coefficients of polyalphaolefins (oligomer composition not specified) exceeded the upper limit of 8.0 that could be determined by the applied HPLC-method.

Information on concentrations of Novasol PAO's in animal tissues from exposed organisms, as noted by these authors, is rather scarce. The authors discuss a few results of a recent study of fish sampled at a North Sea Novadril II well site that were cited in M-I information dated January, 1995. No taste or smell was found in any of the fish sampled. Neither did the concentration of Novasol exceed the detection limit of 0.1 mg.kg-1 in any of the fish samples analyzed. No information was provided by the authors as to where, when and how sampling was performed or how many and which species were analyzed. The authors also present that analyses of commercial fish species captured at the drilling sites is obviously of great public interest. Because of the lack of control on exposure of the analyzed individuals to the test chemical, however, a field study showing neither smell, taste nor detectable concentrations, was not considered to yield evidence that the chemical has a low potential for bioaccumulation. Results of Rushing et al. (1991) were also discussed in this report.

Growcock, F.B., S.L. Andrews and T.P. Frederick. 1994. Physicochemical Properties of Synthetic Drilling Fluids. IADC/SPE 27450. Presented at the IADC/SPE Drilling Conference, Dallas, Texas, February 15-18, 1994.

The dispersibility (aqueous phase partitioning) of synthetic fluids in seawater was tested. The dispersibility test consists of shaking equal volumes of seawater and synthetic fluid for 10 seconds followed by a 10 minute equilibration prior to sampling the seawater phase for organic carbon analysis. The test gave the following trend among various synthetic base fluids:

Ester>Di-Ether>>Detergent Alkylate>PAO>LTMO.

This trend was considered by the authors as qualitatively consistent with the trend in the octanol/water partition coefficient, P_{ow}, which ranges from log P_{ow} = 1.69 for the ester to log P_{ow} = 15.4 for the PAO and the LTMO (no data or sources cited). The authors concluded that it is possible for a significant portion of the ester, and perhaps other synthetics as well, to disperse in seawater.

Færevik, I. Undated. Discharges and regulations of synthetic drilling fluids on the Norwegian Continental Shelf and summary of results from ecotoxicological testing and field surveys. Norwegian Pollution Control Authority.

Laboratory testing shows that many of the chemicals in synthetic drilling fluids have a potential for bioaccumulation. Specifically the olefin base fluids show log P_{ow} values well above 7.0. The ester base fluids are unlikely to bioaccumulate, but several of the additives in ester based drilling fluids show log P_{ow} values above 5.0. The molecular weight for both base fluids and additives in synthetic drilling fluids are typically below 600.

The author asserts that existing bioaccumulation tests are not relevant for surface active substances that are commonly present in synthetic drilling fluids. Rather, bioaccumulation should be expressed as the distribution between sediment and water (the sediment:water partition coefficient, log P_{sw}), not as now by the octanol and water coefficient (log P_{ow}). The author states that the potential for bioaccumulation is overestimated due to inadequate methods of calculation.

Because these fluids have such low aqueous solubilities, a concern has been noted that P_{ow} data are less relevant than, perhaps, P_{sw} data. This would provide some measure of the potential for long-term leaching of these materials into sediment pore water with their subsequent availability to benthic infauna and epifauna. This concern is valid, and these data may be worth pursuing because the standard P_{ow} and P_{sw} protocols appear adequate to evaluate these fluids and are relatively brief and inexpensive procedures. Also, standard experimental protocols for

measuring uptake in test species are available and would be useful for testing a subset of materials for which log P_{ow} or P_{sw} determinations have been performed to confirm bioaccumulation potentials projected from P_{ow} or P_{sw} data.

Environment & Resource Technology. 1994a. Bioaccumulation Potential of ISO-TEQ Base Fluid. ERT 94/209. Prepared for Baker Hughes INTEQ.

The bioaccumulation potential of ISO-TEQ base fluid, an internal olefin of chain length from 16 to 18 carbon atoms (C16-C18), was evaluated. The bioaccumulation potential was estimated by measuring the log octanol-water partition coefficient by HPLC following OECD 117 guidelines. Under the standard conditions described in the report, no elution of the test substance occurred during a period of 6.5 hours. To enhance the elution of the test substance, it was re-examined using 2-propanol:water. The absence of detectable HPLC peaks with the standard system indicated that the log P_{ow} value for ISO-TEQ base fluid was greater than the value for the most lipophilic calibration standard, suggesting that the value would be greater than 9.

Environment & Resource Technology. 1994b. Bioconcentration Assessment Report, Assessment of the bioconcentration factor (BCF) of ISO-TEQ base fluid in the blue mussel Mytilus edulis. *ERT 94/061. Prepared for Baker Hughes INTEQ.*

The study was conducted in accordance with an SOP written to conform with OECD guidelines 305 A-E for the determination of bioconcentration or bioaccumulation of chemicals from the aqueous phase. Specimens of the blue mussel *Mytilus edulis* were exposed to saturated aqueous concentrations of ISO-TEQ base fluid (a predominantly C16-C18 internal olefin) under flow-through conditions for ten days, and subsequently allowed to depurate in clean seawater for a further 20 days. BCF values were calculated from uptake and depuration rates or each compound group separately. The bioconcentration factors (BCF) were calculated from

- the ratio of tissue (lipid) concentration to water concentration of the major components of the fluid at equilibrium (10 days), or if a steady-state was not achieved,

- the ratio of the uptake to depuration rate constants, calculated as defined in the SOP.

The test met all validity criteria, with the exception of exposure concentration control, which varied more than specified as a consequence of the very low saturation concentrations of the test substance components. The variation was not, however, of a magnitude sufficient to significantly affect the estimated low BCF values. ISO-TEQ exhibited high rates of uptake and depuration, with no detectable tissue residue. The equilibrium log BCF values (lipid weight basis) for the test substances were estimated to be 5.37 for the C16 compounds and 5.38 for the

C18 compounds. After cessation of exposure, the test animals depurated their tissues to concentrations of test compound to < 1 ug.g-1 (0.03% of peak value). Log BCF values were approximately half the probable log P_{ow} values (>8).

Jones, F.V., Rushing, J.H., and M.A. Churan. 1991. The Chronic Toxicity of Mineral Oil-Wet and Synthetic Liquid-Wet Cuttings on and Estuarine Fish, Fundulus grandis. *SPE 23497. Presented at the First International Conference on Health, Safety and Environment, The Hague, The Netherlands, November 10-14, 1991.*

Mud minnows (*Fundulus grandis*) were held in tanks of synthetic seawater (i.e., formulated from a mixture of salts and substances that mimic natural seawater). Drilling fluids were prepared using a 80/20 ratio of mineral oil/water for a 7.4 pounds per gallon (ppg) drilling fluid (MOBF) and a 70/30 ratio of PAO/water for an 11.0 ppg drilling fluid (PAO-SBF). Both drilling fluids were then hot-rolled for 16 hours at 66ºC. Each drilling fluid was added to a container of dried cuttings, hand-mixed, and hot-rolled for another 24 hours at 66ºC. Laboratory bioaccumulation tests showed that the presence of cuttings soaked in an 11.0 ppg 70/30 PAO-SBF system did not affect the growth rate of this species. Rather, they showed equal or better weight gain and size increase as compared to the control samples. Conversely, test runs using MOBF-soaked cuttings showed a retarded growth rate with respect to the control. The authors also offered that fish cultured with the mineral oil had to spend a large portion of their energy removing this hydrocarbon from their blood stream, and that this energy drain may have caused the lower observed growth in those fish in the MOBF tanks.

Zevallos, M.A., J. Candler, J.H. Wood and L.M. Reuter. 1996. Synthetic-Based Fluids Enhance Environmental and Drilling Performance in Deepwater Locations. SPE 35329. Presented at the SPE International Petroleum Conference & Exhibition of Mexico, Villahermosa, Tabasco, Mexico, March 5-7, 1996.

Measurement of bioaccumulation of synthetic fluids can be estimated using the N-octanol/water partition coefficient (P_{ow}). P_{ow} values less than three or greater than seven would indicate that the test material will not bioaccumulate. Both the 11.19 P_{ow} for PAO and 8.57 P_{ow} for IO indicate these synthetic materials would not bioaccumulate. Ranked by their P_{ow} values, IOs have a greater potential than PAOs to bioaccumulate.

Davies, J.M., D.R. Bedborough, R.A.A. Blackman, J.M. Addy, J.F. Appelbee, W.C. Grogan, J.G. Parker and A. Whitehead. 1989. The Environmental Effect of Oil-based Mud Drilling in the North Sea. In: Drilling Wastes, F.R. Engelhardt, J.P Ray and A.H. Gillam (eds). Elsevier Applied Science, New York. Pp. 59-89

During 1985 and 1986, fish were caught from three areas in the North Sea close to oil and gas exploration and production platforms and from areas outside the influence of drilling activity as reference (control) samples. These operations had drilled many wells using OBM, including both diesel oil- and mineral oil-based OBMs. Fish were tasted by a trained panel to determine the presence of any oily taint in the flesh. A fish was deemed to be oil tainted if more than half the panel detected an oily taint. Among cod, haddock, tusk, and dabs caught between 0.40 and 9.3 km from oil platforms, only for dabs caught between 0.55 km and 0.86 km did more than half the panel detect an oily taint.

Rushing, J.H., M.A. Churan, and F.V. Jones. 1991. Bioaccumulation from Mineral Oil-Wet and Synthetic Liquid-Wet Cuttings in an Estuarine Fish, Fundulus grandis. *SPE 23497. Presented at the First International Conference on Health, Safety and Environment, The Hague, The Netherlands, November 10-14, 1991.*

The authors report an experimental study on uptake of low aromatic mineral oil (LTMO) and Novasol PAO in tissue and gut samples from mud minnows (*Fundulus grandis*) exposed for 30 days to water equilibrated with contaminated cuttings at nominal concentrations of 1%, 5%, and 8.4% base fluid (i.e., PAO or mineral oil). Gut samples represented carefully excised internal organs and connecting structures from the mouth to the anus. Muscle tissue samples were prepared from fish whose heads, tails, skin, and viscera were removed, thus including finer bones in these samples. Samples from each of the three dosings were taken seven times during the course of the exposure (Days 3, 7, 10, 15, 20, 25, and 30) and again after a 4-day depuration period.

Among fish exposed to SBM-coated cuttings, analysis of fish tissue and organs using GC/MS measured no uptake of PAO in samples of fish tissue, and an accumulation of PAO was observed in only one of 24 gut samples. By contrast, fish exposed to LTMO cuttings showed accumulations of mineral oil in 19 of 24 fish gut samples and detectable amounts of mineral oil components in 12 of the 24 tissue samples analyzed. Both mineral oil and olefins were shown present in the water of the aquaria throughout the exposure period.

The authors concluded that the contrast between the mineral oil and the polyalphaolefins was a result of restricted uptake of the larger olefin molecules across gill and digestive structures. The authors further assert that the high molecular weight and the structure of PAOs is a key factor in limiting the amount of uptake by fish. Since PAOs are a complex, high molecular

weight molecule, fish could not uptake the material through its gill structure. One sampling showed a low amount of PAO in the gut analysis. It is possible this material was in the intestinal tract of the fish and had not passed through the fish when sampled.

8. BIODEGRADATION

8.1 Introduction

A number of different and contrasting test methods have been used to predict the biodegradability of synthetic base fluids deposited on offshore marine sediments. These method variations have included: calculation of biochemical oxygen demand in inoculated freshwater aqueous media versus uninoculated seawater aqueous media; determination of product (gases) evolved versus the concentration of synthetic base fluid remaining at periodic test intervals; varying initial concentrations of test material; aqueous versus sediment matrices; and within sediment matrices, layering versus mixed sediment protocols.

In the field, the mechanisms observed from the deposition of SBF contaminated drill cuttings involve the initial smothering of the benthic community followed by organic enrichment of the sediment due to adherent drilling fluids. Organic enrichment causes oxygen depletion due to the biodegradation of the discharged synthetic base fluids. This biodegradation results in predominantly anoxic conditions in the sediment, with limited aerobic degradation processes occurring at the sediment:water column interface. Therefore, the biodegradation of deposited drilling fluid will be an anaerobic process to a large degree. Standardized tests that utilize aqueous media, while readily available and easily performed, may not adequately mimic the environment in which the released synthetic base fluid is likely to be found and degraded. As a result, alternative test methods have been developed that more closely simulate seabed conditions. One method uses a deposition of synthetic base fluid on marine sediment and measuring degradation in a sediment matrix. Another method uses anaerobic conditions in aqueous media (Vik et al., 1996b; Limia, 1996; Munro, 1997).

8.2 Biodegradation Test Methods

A variety of test methods, each with characteristic limitations and qualifications, has been used to assess the biodegradation of test materials. Slater et al. (1995) present a descriptive comparison of the technical details of the Organization for Economic Co-operation and Development (OECD) 301-series test protocols, the Biochemical Oxygen Demand for Insoluble Substance (BODIS) protocols, and seabed simulation test protocols.

The OECD 301-series tests are all aqueous freshwater tests that use an activated sewage sludge inoculum. As an example of 301 protocols, the OECD 301D “Clean Bottle” test protocol is briefly summarized in Exhibit 8-1. The 301A through 301F tests vary in the analytical endpoint used to quantify oxygen demand, the concentration range of the test substance, and their

design suitability among poorly soluble, volatile, or adsorbing test substances. The drawbacks of using these tests for synthetic base fluids are: the insolubility of synthetic base fluids in aqueous media, the use of a freshwater matrix, the use of an aqueous matrix for the test, and the aerobic nature of the test.

Exhibit 8-1. OECD 301D: 28-Day Closed Bottle Test

A solution of test substance (e.g., synthetic base fluid) is prepared in a mineral medium consisting of stock solutions of a) KH_2PO_4, K_2HPO_4, $Na_2HPO_4 \cdot 2H_2O$, NH_4Cl; b) $CaCl_2$; c) $MgSO_4 \cdot 7H_2O$; and d) $FeCl_3 \cdot 6H_2O$. The test solution is poured into test bottles and inoculated with a small number of micro-organisms derived from the secondary effluent of a domestic sewage treatment plant (or laboratory-scale unit) or surface water. A parallel series of bottles containing inoculated blank medium is prepared for reference measurements of oxygen uptake by the inoculum. The closed test bottles are incubated in the dark at constant temperature for 28 days. Dissolved oxygen measurements are taken via Winkler titration or oxygen electrode at time zero and weekly intervals; more frequent intervals require more bottles. The percent degradation of the test substance is calculated as the ratio of the biochemical oxygen demand of the test substance (in mg O_2 uptake per mg test substance) and the theoretical oxygen demand (or less accurately, the chemical oxygen demand) of the test substance.

The OECD 306 methods change the matrix from a freshwater matrix to a seawater matrix, and allow for two analytical variants. In one analytical variant, the incubation period increases from 28 days to 60 days. The biggest difference between the OECD freshwater and seawater tests is the presence of an activated sludge inoculum in freshwater tests versus the absence of an inoculum in the seawater tests, which relies on endogenous marine microorganisms for degradative capacity.

Two International Standards Organization (ISO) protocols, one for freshwater (BODIS/FW) and one for seawater (BODIS/SW), also have been used to assess biodegradability of insoluble test materials. The same characteristics as discussed for the OECD 301 methods regarding the presence/absence of a sludge inoculum apply to these ISO protocols: the freshwater test uses inoculum but the seawater test does not. Likewise, freshwater and seawater respirometric methods, which rely on analytically different endpoints, can be characterized as similar to the 301-series tests. An ISO protocol for assessing freshwater anaerobic biodegradability is available (see Exhibit 8-2 for a brief description). The protocol may more accurately assess real-world conditions for a large portion of discharged synthetic base fluids. However, although this protocol provides a quantification of anaerobic biodegradation, it still relies on an aqueous freshwater matrix.

Exhibit 8-2. ISO 11734: "Water Quality--Evaluation of the "Ultimate" Anaerobic Biodegradability of Organic Compounds in Digested Sludge--Method by Measurement of the Biogas Production"

A test compound (e.g., synthetic base fluid) is added to a dilution medium at an organic carbon concentration of 20 mg/l to 100 mg/l. The dilution medium is a solution of the following constituents: KH_2PO_4, $Na_2HPO_4 \cdot 12H_2O$, NH_4Cl, $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, $Na_2S \cdot 9H_2O$, resazurin (oxygen indicator), stock solution of trace elements, and de-oxygenated water. Under anaerobic conditions, the test solution is inoculated with washed digested sludge containing very low amounts of inorganic carbon, then incubated in sealed vessels in the dark at constant temperature for 60 days.

As a result of anaerobic degradation, carbon dioxide and methane evolve in the headspace above the test solution, and the amount of dissolved carbon dioxide, hydrogen carbonate, or carbonate in the solution increases. The amount of microbiologically produced carbon in the head space gas is calculated from the measured increase in head space pressure as applied to the gas law equation (PV=nRT). The amount of inorganic carbon produced in the solution is measured, and is added to the amount of head space carbon to determine the total carbon produced in excess over blank values. The percentage biodegradation is calculated as the total carbon produced relative to the initial carbon in the test compound.

The progress of biodegradation can be charted by intermediate measurements of head space pressure. A graph of pressure versus time should show an initial lag phase followed by a period of steadily increasing pressure, ending with a plateau phase indicating the cessation of gas production. Significant deviations from this course may indicate that the test should be prolonged or repeated.

To address the issue of aqueous versus sediment matrices, two non-standard test protocols have been developed. One, the "NIVA" protocol (Norwegian Institute for Water Research; Schaanning, 1994), which is commonly referred to as the "simulated seabed study," relies on layering of test material on the surface of the test sediment. The other is the "SOAEFD" test protocol (Scottish Office, Agriculture Environment and Fisheries Department; Munro et al., 1997b), which is commonly referred to as the "solid phase test," mixes the test material into the test sediment prior to incubation (see Exhibits 8-3 and 8-4 for brief descriptions of the NIVA and SOAEFD protocols). These laboratory protocols, to date, have assessed biodegradability of synthetic fluids at experimental sediment levels (NIVA = 700 mg/kg to 18,000 mg/kg; SOAEFD = 100 mg/kg to 5,400 mg/kg) that are below or at the lower end of the range of sediment concentrations of synthetic fluids measured in the field at two drill sites in the North Sea (up to 4,700 mg/kg and up to 100,000 mg/kg) and one drill site in the Gulf of Mexico (up to 134,000 mg/kg, or 13.4 percent).

Exhibit 8-3. NIVA Protocol for Simulated Seabed Biodegradation Study

NIVA protocols have evolved since 1990, and intend to more accurately represent offshore seabed conditions for biodegradation. The test consists of a series of chambers containing clean sediment, covered with 15 cm of seawater drawn from a depth of 60 m from the Oslofjord and pumped through the experimental chambers. On Day 0, a thin layer of drill cuttings (1-2 mm) is created by adding a slurry to the chamber water and allowing particulates and solids to settle. Tests run for as long as 160 days.

Based on the measured amounts of fluid at Day 0 and the last day of the test, the percentage decrease is calculated. Rates are adjusted for the loss of drilling fluid due to seawater flow by using Ba concentrations as an indicator for test substance lost due to seawater flow-through. NIVA has found that first-order kinetics describe the loss of drilling fluid over time according to

$$C_t = C_0 \times 10^{-kt}$$

where C_t =test substance concentration at time *t* (in days), C_0 = the concentration at *t = 0*, *k* is the decay constant, and *t* is the time in days.

Exhibit 8-4. SOAEFD Protocol for Solid-Phase Test System for Degradation of Synthetic Base Fluid

A synthetic base fluid is homogeneously mixed at specific concentrations with prepared marine sediment and maintained in a trough of flowing sea water for 120 days. Base fluid is added at concentrations of 100 ppm, 500 ppm, and 5,000 ppm to represent historical measurements of mineral-oil-based cuttings piles at distances from the platform of 1,000 m to 3,000 m, 200 m to 1,000 m, and 200 m, respectively. The concentrations of added base fluid are determined empirically prior to the experiment as µg TOC per g of dry sediment.

At set times, triplicate jars are removed for chemical analysis of the base fluid. The concentration of the base fluid remaining is determined by solvent extraction followed by gas chromatography with flame ionization detection. Base fluid concentrations (in ppm) are graphed as a function of time; results are compared in terms of how closely the data follow first order reaction kinetics, as expressed by the equation:

$$A_t = A_0 e^{-kt}$$

where A_0 is the concentration of the substance at time t = 0, A_t is the concentration at time t, k is the rate constant for the reaction and e is the log to the base e.

Three additional analyses are conducted to further characterize the course of biological activity throughout the experiment: the oxidation-reduction (redox) profiles of the test sediments as compared with clean sediment; the number of culturable bacteria from sediments; and the number of bacteria capable of growth on the test fluid as the sole carbon source (the Sheen-screen). The sediment redox profiles, expressed in mV, measure the level of oxygenation of the sediment at varying depths, indicating the local concentration of organic matter. Trends in redox measurements are charted by depth and over time, for temporal and spacial comparisons between test sediments and clean sediment. Throughout the experiment, samples are taken at the sediment surface and at a depth of 4 mm to measure the number of "culturable" aerobic and anaerobic bacteria. The Sheen-screen measures the number of aerobic and facultative anaerobic bacteria per gram of wet sediment capable of growth on the synthetic base fluid as the sole carbon source. It is an indicator for the biodegradation potential of a base fluid in the sediment used. The conditions for the Sheen-screen are aerobic and thus, growth of obligate anaerobes is not provided for and test conditions do not accurately mimic real world conditions for discharged synthetic drilling fluids.

Aerobic test conditions have been summarized by Vik et al. (1996b) and are presented in Exhibit 8-5; a summary of laboratory and field biodegradation assessment procedures were summarized by Vik at al. (1996b) and are presented in Exhibit 8-6.

8.3 Biodegradability Results

Two overarching concerns in any presentation of data on biodegradation of synthetic base fluids are the incompatibility of test results obtained using different protocols and the high variability routinely encountered within a given protocol. These two factors mitigate against the utility of the data in any comparative sense. Additionally, the differences in fresh- versus saltwater media, aerobic versus anaerobic media, and aqueous versus sediment matrices render the applicability of most of the reported tests as extremely limited. Sedimentary phase tests are more comparable to the actual conditions in which these materials will be found and provide more consistent results than aqueous phase tests.

8.3.1 *Aqueous Phase Tests*

Exhibit 8-7 presents a ranking of aerobic biodegradation test results for an acetal synthetic fluid using OECD 301B (FW), 301D (FW), 306 (SW), BODIS (FW), and BODIS (SW) protocols at two concentrations of added test material. Given the substantial differences in experimental design and protocols, results of 28-day tests expectantly show a wide range in results, from 5% degradation to 86% degradation. Degradation was, as expected for a system subject to saturation kinetics, more extensive for any given protocol at the lower test concentrations (although with one exception). Few other comparisons are meaningful. For example, seawater tests show less degradation than freshwater tests. Thus, BODIS seawater tests show less degradation (8% and 19.5% at 40 mg/l and 10 mg/l, respectively) than BODIS freshwater tests (50% and 86% at 40 mg/l and 10 mg/l, respectively). Similarly, the OECD 306 seawater test at all concentrations shows less degradation compared to either the OECD 301B or 301D freshwater tests at the same test concentration. However, the freshwater tests all use an activated sewage sludge inoculum of microorganisms, whereas the seawater tests are endogenous levels of microorganisms, with no exogenous addition of microbial degraders. Because the initial degradative capacity of the two types of media are not comparable, no valid quantitative comparisons are possible.

Within laboratory variability also is high for these tests. Exhibit 8-8 presents BODIS aerobic freshwater and seawater results at one laboratory for two synthetic fluids (an ester and an acetal). The pooled, average relative standard deviation (RSD) for four freshwater tests of each

Exhibit 8-5. Summary of Aquatic Phase Aerobic Laboratory Biodegradation Test Conditions and Their Suitability for Poorly Soluble, Volatile, and Surface Active Compounds

OECD Guidelines/ ISO Procedures (a)	Analytical Method	Suitability for compounds which are:			Concentration of Test Substance	Inoculum	Test Duration (days)	Test Medium
		Poorly Soluble (b)	Volatile	Adsorbing (b)				
OECD 301A - DOC Die-Away	Dissolved organic carbon (DOC)	-	-	+/-	10-40 mg DOC/l	+	28	FW
OECD 301B - CO_2 Evolution Test	CO_2 evolution	+	-	+	10-20 mg DOC/l	+	28	FW
OECD 301C - MITI (l) Test	Oxygen consumption	+	+/-	+	100 mg/l	+	28	FW
OECD 301D - Closed Bottle Test	Dissolved oxygen	+/-	+	+	2-5 mg/l	+	28	FW
OECD 301E - Modified OECD Screening Test	Dissolved organic carbon	-	-	+/-	10-40 mg DOC/l	+	28	FW
OECD 301F - Manometric Respirometry Test	Oxygen consumption	+	+/-	+	50-100 mg ThOD/l	+	28	FW
OECD 308 - Biodegradability in seawater								
- Shake Flask Test	Dissolved organic carbon	-	-	+/-	5-40 mg DOC/l	-	60	SW
- Closed Bottle Test	Dissolved oxygen	+/-	+	+	2-10 mg/l	-	28	
ISO-procedure: BOD-test for insoluble substances (BODIS)	Dissolved oxygen	+	-	+/-	100 mg ThOD/l (c)	+	28	FW
Modified Seawater BODIS Test	Dissolved oxygen	+	-	+/-	100 mg ThOD/l (c)	-	28	SW
Respirometric methods	Respirometric: CO_2-production O_2-consumption in headspace	+	+/-	+	100 mg ThOD/l (and lower) (c)			SW/FW

Abbreviations: ThOD = Theoretical oxygen demand; BOD = biochemical oxygen demand

(c) OECD (1993); ISO (1990)

(d) Characteristics of synthetic base fluids

(e) Corresponds to ~ 30 mg/l test substance of drilling fluids

Source: Vik et al., 1996b

Exhibit 8-6. Summary of Test Procedures Used in the Biodegradation Testing of Synthetic-Based Drilling Fluids

Factors influencing test results	Aqueous Phase Tests			Sedimentary Phase Studies		Seabed Surveys		
	Aerobic		Anaerobic					
	Seawater (a)	Fresh-water	Fresh-water	NIVA "Seabed Simulation"	SOAEFD "Solid Phase"	Norwegian sector	Dutch sector	Gulf of Mexico
Test Substance	**Base fluid or Synthetic Fluid**	**Base fluid or Synthetic Fluid**	**Base fluid or Synthetic Fluid**	**Cuttings**	**Base fluid**	**Cuttings**	**Cuttings**	**Cuttings**
Physical test conditions: Temperature ºC	15-20	15-25	37	7-12	7-12	7-12	7-12	7-12
Availability of oxygen	Good	Good	None	Lower dependent on test concentration	Very low	Very low	Very low	Very low
Nutrient availability	Good	Good	Good	May be limiting	May be limiting	May be limiting	May be limiting	May be limiting
Test concentration	2-40 mg/l	0.5-40 mg/l	50 mg/l	700-18000 mg/kg	100, 500, 5000 mg/kg	up to 100,000 mg/kg	up to 4700 mg/kg	up to 134,000 mg/kg
Depth of mud layer	Not applicable	Not applicable	Not applicable	1-2 mm	Mixed into the sediment	0-20+ cm	0-20+ cm	0-20+ cm
Migration of test substance	Not applicable	Not applicable	Not applicable	Possible	Very low	Very probable	Extensive	Extensive
Inoculum: Quantity/density	Low	Generally high	High	Fairly low	Fairly low	Fairly low	Fairly low	Fairly low
Variability	High	Lower than seawater	Lower than seawater	High	High	High	High	High
Acclimation	None	None	None	Some	Some	Some	Some	Some
Source	Seawater	Activated sludge	Activated sludge	Seawater and mixed sediments (b)	Seawater and mixed sediments	Seawater and natural benthic fauna	Seawater and natural benthic fauna	Seawater and natural benthic fauna
Renewal	None	None	None	Possible	Possible	Very likely	Very likely	Very likely

Exhibit 8-6. Summary of Test Procedures Used in the Biodegradation Testing of Synthetic-Based Drilling Fluids (continued)

Factors influencing test results	Aqueous Phase Tests			Sedimentary Phase Studies		Seabed Surveys		
	Aerobic		Anaerobic					
	Seawater (a)	Fresh-water	Fresh-water	NIVA "Seabed Simulation"	SOAEFD "Solid Phase"	Norwegian sector	Dutch sector	Gulf of Mexico
Test Substance	**Base fluid or Synthetic Fluid**	**Base fluid or Synthetic Fluid**	**Base fluid or Synthetic Fluid**	**Cuttings**	**Base fluid**	**Cuttings**	**Cuttings**	**Cuttings**
Sampling/analyses: Sampling depth	Not relevant	Not relevant	Not relevant	1-2 cm	8.6 cm (c)	1 cm	10 cm	up to 1 m
Chemical analyses	Oxygen demand/CO_2	Oxygen demand/CO_2	CO_2	Presence of base fluid/DO/pH/redox	Presence of base fluid/DO/redox	Presence of base fluid	Presence of base fluid	Presence of base fluid
Macrofaunal analyses	None	None	None	Mortality on surface (d)	None	Abundance and diversity	Abundance and diversity	Abundance and diversity
Microbial analyses	No	No	No	Yes	Yes			
Relevance of test to real environment	Aerobic degradation only	Not relevant	Not relevant	Relevant, but test concentrations are lower; question anaerobic condition simulation and test substance migration	Relevant; dosing more stable but misses layering as in situ	Relevant. Difficult to obtain representative samples and compatible results from one year to another	Relevant. Difficult to obtain representative samples and compatible results from one year to another	Relevant. Difficult to obtain representative samples and compatible results from one year to another

(a) No standard marine test presently exists and a large variety of methods have been used.
(b) In the latest NIVA test, natural benthic fauna were sieved out, then returned.
(c) NIVA are presently trying an alternative procedure using undisturbed sediments to keep the macro-fauna alive.
(d) Comprises the entire test container contents.
DO = dissolved oxygen
Adapted from Vik et al., 1996b

Exhibit 8-7. Ranking of Aqueous Phase Biodegradation Methods and Test Results

No.	Test Method	Test Concentration	% Biodegradation
1	BODIS Freshwater	10 mg/l	86
2	OECD 301 B Freshwater	10 mg/l	78.6
4	OECD 301 B Freshwater	20 mg/l	62.8
5	BODIS Freshwater	40 mg/l	50
6	OECD 306 Seawater	0.5 mg/l	35
3	OECD 301 D Freshwater	0.5 mg/l	73
7	OECD 301 D Freshwater	2.5 mg/l	21
8	BODIS Seawater	10 mg/l	19.5
9	OECD 306 Seawater	10 mg/l	9.4
10	BODIS Seawater	40 mg/l	8
11	OECD 306 Seawater	2 - 2.5 mg/l	5

Source: Slater et al. (1995)

Exhibit 8-8. Average Percentage Biodegradation Using BODIS Seawater and Freshwater Procedures for an Ester and Acetal

Base fluid	Seawater tests					Freshwater tests				
	Test # (a)	Biodeg. (%)	s.d. (%) (b)	Relative s.d. (%) (c)	n	Test # (a)	Biodeg. (%)	s.d. (%) (b)	Relative s.d. (%) (c)	n
Ester	1	41	8.1	18	5	1	68	3.1	5	4
	2	32	2.9	9	5	2	94	11.2	12	4
	3	29	7.1	24	5	3	94	9.9	11	7
	4	34	3.7	11	5	4	99	1.9	2	10
	5	57	5.2	9	5					
	6	59	5.0	8	5					
	Pooled average	42	12.9	31	30	Pooled average	92	12.9	14	25
Acetal	1	9	2.2	24	5	1	58	10.7	18	4
	2	5	1.2	24	5	2	69	9.1	13	5
	3	9	1.8	20	5	3	75	12.0	16	7
	4	11	2.8	25	5	4	95	4.9	5	10
	5	37	4.7	13	5					
	6	12	7.1	59	5					
	Pooled average	14	11.2	80	30	Pooled average	79	16.5	21	26

(a) # = number of parallels
(b) s.d. = standard deviation
(c) relative s.d. = defined as (s.d./biodeg) x 100%
Source: Vik et al. (1996b)

base fluid was 14% for the ester (n=25) and 21% for the acetal (n=26). For six seawater tests, however, the RSD increased to 31% (n=30) and 80% (n=30), respectively for the ester and acetal.

Anaerobic results, although more relevant to the potential impacts of synthetic base fluids in marine receiving waters, show even greater variability for many types of synthetic base fluids (Exhibit 8-9). For example, fatty acid esters or alcohols showed significant anaerobic degradation potential, with degradation ranging from 79% to 89% with RSDs of less than 25%. However, degradation rates ranged from -1.5% to 48% for 13 mineral oils and 8 other synthetic fluids. Furthermore, RSDs were much higher, with a minimum RSD of 80% and all others well in excess of 100%.

8.3.2 *Sedimentary Phase Tests*

Schaanning (1994; 1995; 1996a; and 1996b) reported on a series of studies using the NIVA methods (Exhibit 8-3) to compare the biodegradation rates (half-life) of ester, IO, LO,PAO and ether base and based fluids. The results from the studies indicated the following degradation rates esters>LO>IO>PAO>ethers. The half-lifes reported were esters ranged from 16 to 22 days, LO half-life reported was 51days, IO half-life reported was 73 days, PAO ranged from 43 to 207 days, and the ethers ranged from 254 to 536 days.

Vik et al. (1996b) compare the results of two sedimentary phase protocols (NIVA and SOAEFD) for ester-type synthetic fluids (Exhibit 8-10). An ester-type synthetic base fluid was degraded 46% and 97% at 28 days and 160 days, respectively, in the NIVA protocol, with a calculated half-life of 31 days. The SOAEFD protocol for a similar synthetic base fluid resulted in 97% degradation at 28 days with no further measured degradation at 60 days, giving a calculated half-life of 12 days. Experimental differences, as discussed earlier, are substantial enough that any comparison is not very meaningful. Vik et al. (1996b) also report results of the NIVA protocol (see Exhibit 8-10) across a variety of synthetic fluids and mineral oil. Their results indicate the ester and LAO fluids (respective half-lives of 31 and 43 days) degrade more rapidly than the PAO, acetal, and mineral oil (half-lives ranging from 199 - 207 days). This general trend was also observed in the solid phase tests, at least for the lower test concentrations.

Limia (1997) reports solid phase degradation data for a series of test substances that included an ester, acetal, PAO, IO, LAO, n-paraffin, and mineral oil. Results suggested relative degradation rates were dependent on initial concentrations. At the highest concentration (5,000

Exhibit 8-9. Anaerobic Biodegradability of Test Chemicals Examined in the ECETOC Screening Test (a)

Test Chemical	Test Duration (days)	Degradation in the ECETOC test (% of organic carbon)		
		Net gas Production	Net DIC (b) Production	Extent of Ultimate Degradation (c)
fatty acid ester I	35	63.3	19.2	82.5±13.9
fatty acid ester II	35	61.2	22.5	83.7±13.1
Oleyl alcohol	84	61.1	27.5	88.6±14.8
2-Ethyl hexanol	84	57.3	21.5	78.8±21.4
Mineral oil A	35	0.7	3.2	3.9±11.0
Mineral oil B	28	4.3	1.1	5.4±8.2
Mineral oil C	28	3.8	2.0	5.8±6.7
Di-octyl ether	42	8.8	3.5	12.3±10.8
Di-hexadecyl ether	42	-0.6	1.9	1.4±12.5
linear ∝-olefin ($C_{16/18}$)	84	22.3	0.1	22.4±19.5
linear ∝-olefin (C_{14})	98	40.5	7.8	48.3±15.5
Polyalphaolefin I	70	4.4	10.0	14.4±20.3
Polyalphaolefin II	50	-1.6	2.2	0.6±16.2
Alkylbenzene	50	0.9	-2.4	-1.5±12.2
Acetal-derivative	70	3.7	8.9	12.6±19.2

(a) ECETOC = European Centre for Ecotoxicology and Toxicology of Chemicals
(b) DIC = Dissolved Inorganic Carbon
(c) Value reported is mean value (from 5 replicates) and its 95%-confidence interval
Source: Steber et al. (1995)

mg/kg) the ester, LAO, and acetal all showed substantial degradation (25 - 50%; ester>acetal>LAO) after 120 days, whereas all other base fluids tested showed little degradation. At 500 mg/kg, degradation of the ester was nearly 60%, whereas all of the other base fluids degraded much less. At 100 mg/kg, only the ester, LAO, IO, and n-paraffin all degraded substantially (>75%), whereas the other test materials (mineral oil, PAO, and acetal) did not show more than 35% degradation. Similarly, Munro et al. (1998) reported degradation rates using the SOAEFD method that were highly concentration dependent as well as sediment dependent. The half-life for all compounds tested (olive oil, mineral oil, ester, and PAO-LAO blend) increased with concentration and from mud to sand.

Exhibit 8-10. Percentage Biodegradation of Base Fluids in Drilling Fluids Measured by Various Test Methods

Drilling Fluid/Base Fluid Tested	% Biodegradation Measured by Sedimentary Phase Test Methods					
	NIVA's Seabed Simulation Studies (layered using drilling fluid)			SOAEDF's Solid-Phase Sediment Test (base fluid/sand mixture)		
	160-day	28-day	Half-life (days) (a)	60-day	28-day	Half-life (days)
An ester	97	46	16, 20, 22	67[b], 97[c], 98 (d) 98, 78, 25 (e)	97	37 (b), 12 (c), 10 (d)
A mineral oil	44	23	399	16, 10, -4 (e)		
A PAO	43	11	43, 127, 207	-11, 4, 8 (e)		
An acetal	39	12	200	20, 0, 10 (e)		
An IO			73	60, 10, -2 (e)		
An LAO	93	38	43	70, 23, 5 (e)		
An LO			51			
An ether			254, 392, 536			

(a) Values from Schaanning (1994, 1995, 1996a & 1996b)
(b) Mixed in mud substrate; Munro et al. (1997)
(c) Substrate not specified in Vik et al. (1996)
(d) Mixed in sand substrate; Munro et al. (1997)
(e) Three values presented are day 56 values at 100 mg/kg, 500 mg/kg, and 5,000 mg/kg sediment substrates, respectively; Munro et al. (1997)

Source: Adapted from Vik et al. (1996b)

8.4 Discussion and Conclusions

The result of this review is that the current state of knowledge for these materials is as follows:

- All synthetic fluids have high theoretical oxygen demands (ThODs) and are likely to produce a substantial sediment oxygen demand when discharged in the amounts typical of offshore drilling operations.

- Existing aqueous phase laboratory test protocols are incomparable and results are highly variable. Sedimentary phase tests are less variable in their results, although experimental differences between the "simulated seabed" and "solid phase" protocols have resulted in variations between test results.

- There is disagreement among the scientific community as to whether slow or rapid degradation of synthetic base fluids is preferable with respect to limiting environmental damage and hastening recovery of benthic communities. Materials which biodegrade quickly will deplete oxygen more rapidly than more slowly degrading materials. However, rapid biodegradation also reduces the exposure period of aquatic organisms to materials which may bioaccumulate or have toxic effects.

- Limited field data suggest these materials will be substantially degraded on a time scale of one to a few years; however, the distribution and fate of these materials is not extensively documented, especially as applicable to the Gulf of Mexico where only three field studies have been conducted.

The limited data from field studies suggest that organic enrichment of the sediment will be a dominant impact of SBF-cuttings discharges. Biodegradability of these materials is therefore an important factor in assessing their potential environmental fate and effects.

Available standard methods yield results that are highly variable across available freshwater and seawater protocols. These methods (all aqueous, most freshwater, and all but one aerobic) also are not very relevant to the conditions under which discharged materials will be found (i.e., a largely anoxic, marine sediment matrix). Nonetheless, one could try to identify tests that, despite these shortcomings, still could offer useful insight into the potential fate of these materials. Unfortunately, field data for which potential correlations could be examined are too scant for meaningful quantitative analyses to these standard laboratory methods.

Seabed simulation protocols and solid-phase tests have been developed to better represent receiving water conditions. Still, the issue of layering versus sediment mixture of test substances cannot be resolved absent better field data of actual initial deposition and longer term sediment depth profiles of these materials in discharged cuttings. It seems likely the real world situation is a mixture of the two.

Each of the existing biodegradation test methods has advantages and disadvantages. The seabed simulations better represent field conditions, but they are expensive and have limited market availability. The standard aqueous test methods are not relevant to field conditions, but are more rapid, more widely available, and less expensive. The solid phase test combines the benefits of these two extremes: it mimics receiving water (sediment) conditions, is reproducible, and can be made simplistic enough to perform at moderate expense.